AMENDMENTS

Amendments to the Claims:

This listing of claims will replace all prior versions, and listings, of claims in the application:

Listing of Claims:

1. (currently amended) A process for the production of hydrogen, comprising:

a) reacting steam with a vaporizable hydrocarbon at a temperature of from about 200°C to about 700°C and at a pressure of from about 1 bar to about 200 bar in a reaction zone containing a reforming catalyst to produce a mixture of primarily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide;

b) providing heat to said reaction zone by employing flameless distributed combustion comprising passing a fuel gas through a fuel tube having a plurality of openings or nozzles spaced along the length of the fuel tube thereby driving said reaction;

c) conducting said reaction in the vicinity of a hydrogen-permeable and hydrogen-selective membrane, whereby hydrogen formed in said reaction zone permeates through said selective membrane and is separated from said carbon dioxide and carbon monoxide.

2. (original) The process of claim 1 wherein the vaporizable hydrocarbon is selected from the group consisting of natural gas, methane, methanol, ethane, ethanol, propane, butane, light hydrocarbons having 1-4 carbon atoms in each molecule, light petroleum fractions including naphtha, diesel, kerosene, jet fuel or gas oil, and hydrogen, carbon monoxide and mixtures thereof.

3. (original) The process of claim 1 wherein the flameless distributed combustion used to drive the reaction comprises:

a) preheating either a fuel gas or oxidant or both to a temperature that exceeds the autoignition temperature of the fuel gas and oxidant when they are mixed;

b) passing said fuel gas and oxidant into a heating zone which is in heat transferring contact along a substantial portion of said reaction zone; and

c) mixing the fuel gas and oxidant in said heating zone in a manner that autoignition occurs, resulting in combustion without high temperature flames, thereby providing uniform or tailored, controlled heat over a substantial portion of said heating zone which is in contact with said reaction zone.

4. (original) The process of claim 3 wherein the fuel gas is passed through a plurality of tubes in said heating zone, said tubes having openings sized and spaced to control the quantity of fuel gas mixed with oxidant at various points along the heating zone.

5. (Original) The process of claim 4 wherein the oxidant is air, and the air and fuel gas used for flameless distributed combustion are heated to a temperature between about 1000°F and about 2300°F.

6. (currently amended) The process of claim [6]<u>3</u> wherein the fuel gas is mixed with oxidant in increments so that upon autoignition the temperature of the resulting combustion gas will rise no more than from about 20°F to about 200°F.

7. (original) The process of claim 4 wherein said heating zone substantially surrounds said reaction zone.

8. (original) The process of claim 7 wherein the plurality of tubes in the heating zone are placed in a circular pattern in said heating zone.

9. (currently amended) The process of claim 2 wherein a sweep gas is used to promote the [diffusion] permeation of hydrogen through said membrane.

10. (original) The process of claim 9 wherein the sweep gas is selected from the group consisting of steam, carbon dioxide, nitrogen and condensable hydrocarbons.

11. (original) The process of claim 2 wherein said hydrogen permeable membrane comprises one or more Group VIII metals on a porous ceramic or porous metal support.

12. (original) The process of claim 2 wherein the vaporizable hydrocarbon is methane or methanol.

13. (original) The process of claim 2 wherein the vaporizable hydrocarbon is naphtha at boiling point range of 350-500°F, or diesel, kerosene or jet fuel at boiling point range of 350-500°F, or gas oil at boiling point range of 450-800°F.

14. (original) The process of claim 1 characterized by the use of a reduced steam to vaporizable hydrocarbon ratio without substantial coke formation in said reaction zone heated by said flameless distributed combustion.

15. (original) The process of claim 3 wherein the fuel gas which is mixed with an oxidant and used for flameless distributed combustion is hydrogen.

16. (original) The process of claim 1 wherein said reforming catalyst comprises at least one Group VIII transition metal on a support.

17. (original) The process of claim 1 wherein said membrane has a permeability in the range of 8×10^{-4} to 80 standard cubic meters/m^2/sec/bar$^{1/2}$.

18. (original) The process of claim 11 wherein said hydrogen-permeable membrane comprises Pd or a Pd alloy.

19. (original) The process of claim 1 wherein the temperature in the reaction zone is from about 300°C to about 600°C and the pressure is from about 10 bar to about 50 bar.

20. (original) The process of claim 11 wherein said membrane has a permeability in the range of 8×10^{-3} to 70 standard cubic meters/m^2/sec/bar$^{1/2}$.

21. (original) The process of claim 1 wherein a vacuum is used to promote the diffusion of hydrogen through said membrane.

22. (original) The process of claim 9 wherein the sweep gas is steam.

23. (original) The process of claim 16 wherein said reforming catalyst comprises nickel on alumina.

24. (original) The process of claim 19 wherein the temperature in the reaction zone is from about 400°C to about 500°C.

25. (original) The process of claim 18 wherein the hydrogen-permeable membrane comprises Pd or Pd alloy on a porous stainless steel support.

26. (original) The process of claim 15 wherein the oxidant is air and the hydrogen and air are combusted at a stoichiometric ratio of hydrogen to oxygen of 2:1, resulting in a flue gas stream that has a high concentration of nitrogen on a dry basis.

27. (original) The process of claim 1 characterized in that nitrogen oxide formation in the reaction zone heated by said flameless distributed combustion is at a level below 10 ppm.

28. (original) The process of claim 1 wherein the vaporizable hydrocarbon and steam provides a minimum overall O:C ratio of 2:1.

29. (currently amended) The process of claim 1 wherein the amount of CO in the hydrogen which permeates through [then] <u>the</u> membrane is less than about 10 ppm.

30. (currently amended) The process of claim 29 wherein [the] nitrogen oxide formation in the reaction zone heated by flameless distributed combustion is less than 1 ppm.

31. (original) The process of claim 25 wherein the Pd alloy is selected from the group consisting of an alloy of Pd with 30-50%w copper, an alloy of Pd with 5-30%w silver, an alloy of Pd with 1-10%w yttrium, an alloy of Pd with 1-10%w holmium, an alloy of Pd with 10%w gold, an alloy of Pd with 1-10%w ruthenium and an alloy of Pd with 1-10%w cerium.

32. (original) The process of claim 1 wherein the hydrogen permeable membrane has a thickness in the range of 0.1 to 20 μm.

33. (original) The process of claim 32 wherein the hydrogen permeable membrane has a thickness of 0.5 to 3μm.

34. (currently amended) A process for the production of high purity hydrogen and the use thereof in generating electricity which comprises:

a) reacting steam with a vaporizable hydrocarbon at a temperature of about 200°C to about 700°C and a pressure of from about 1 to about 200 bar in a reaction zone containing reforming catalyst to produce a mixture of primarily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide;

b) providing heat to said reaction zone by employing flameless distributed combustion <u>comprising passing a fuel gas through a fuel tube having a plurality of openings or nozzles spaced along the length of the fuel tube</u> thereby driving said reaction;

c) conducting said reaction in the vicinity of a hydrogen-permeable and hydrogen selective membrane, whereby hydrogen formed in said reaction

zone permeates through said selective membrane and is separated from said carbon dioxide and carbon monoxide; and

d) directing said separated hydrogen to the anode of a fuel cell.

35. (original) The process of claim 34 wherein the fuel cell is a high pressure molten carbonate fuel cell and the non permeable by-product gases from the reaction zone are directed to the cathode of said fuel cell.

36. (original) The process of claim 35, which further comprises the separation and sequestration of high concentrations of carbon dioxide from the process streams and/or from other external CO_2-containing streams.

37. (original) The process of claim 35 wherein nitrogen is obtained as a high purity stream from the outlet of the cathode of a molten carbonate fuel cell.

38. (original) The process of claim 35 wherein the efficiency in the generation of electricity from the vaporizable hydrocarbon starting fuel is 71% or greater.

39. (original) The process of claim 34 wherein the fuel cell is a PEM fuel cell or a solid oxide fuel cell.

40. (currently amended) A steam reforming process for producing high purity hydrogen and CO_2 which comprises:

a) providing a generally tubular reforming chamber having one or more inlets for a vaporizable, hydrocarbon and steam and one or more corresponding outlets for byproduct gases, including H_2O, and CO_2, with a flow path in between said inlet and outlet, and

one or more inlets for sweep gas and corresponding outlets for sweep gas and hydrogen, with a flow path between said inlet and outlet, and

one or more inlets for preheated oxidant and corresponding inlets for fuel gas mixtures, with a flow path between said inlets containing a plurality of flameless distributed combustion heaters,

Wherein said flow path for vaporizable hydrocarbon and flow path for sweep gas forms two concentric sections with an annulus between having a reforming catalyst therein and including a permeable membrane on the inside or outside of the concentric sections;

b) Feeding into said reforming chamber through said one or more inlets a stream of vaporizable hydrocarbon and steam;
c) Flowing said vaporizable hydrocarbon over a reforming catalyst;
d) Causing steam reforming to take place in said reforming chamber; and
e) Conducting said reforming in the vicinity of a hydrogen permeable and hydrogen-selective membrane, whereby pure hydrogen permeates said membrane;
f) Wherein heat to drive said reaction is provided by said flameless distributed [combustors] <u>combustion heaters</u>.

41. (original) The process of claim 40 wherein the temperature in said reforming chamber is from about 200°C to about 700°C.

42. (original) The process of claim 41 wherein the vaporizable hydrocarbon is selected from the group consisting of natural gas, methane, methanol, ethane, ethanol, propane, butane, light hydrocarbons having 1-4 carbon atoms in each molecule, light petroleum fractions including naphtha at boiling point range of 350-500 °F, or diesel, kerosene or jet fuel at boiling point range of 350-500 °F, or gas oil at boiling point range of 450-800 °F, hydrogen, carbon monoxide and mixtures thereof.

43. (original) The process of claim 42 wherein the sweep gas is selected from the group consisting of steam, carbon dioxide, nitrogen and condensable hydrocarbons.

44. (currently amended) The process of claim 40 wherein the flameless distributed combustion used to heat the reforming chamber comprises:

a) preheating either a fuel gas or oxidant or both to a temperature that exceeds the autoignition temperature of the fuel gas and oxidant when they are mixed;

b) passing said fuel gas and oxidant into said [heating section] <u>heaters</u> which is in heat transferring contact along a substantial portion of said reforming chamber; and

c) mixing the fuel gas and oxidant in said [heating section] <u>heaters</u> in a manner that autoignition occurs, resulting in combustion without high temperature flames, thereby providing uniform, controllable heat over a substantial portion of said heating zone which is in contact with said reforming chamber.

45. (original) The process of claim 40 wherein said plurality of flameless distributed combustion heaters are placed in a circular pattern in the outer concentric section.

46. (original) The process of claim 41 wherein said inlet stream of vaporizable hydrocarbon and steam pass into said reforming chamber and into contact with said catalyst and one side of said hydrogen-selective membrane to produce CO_2, CO and H_2.

47. (original) The process of claim 44 further comprising passing a separate stream including steam, carbon dioxide, nitrogen, or condensable hydrocarbon through an inlet adjacent to the opposite side of said membrane in such manner as

to promote hydrogen diffusion through said membrane from one side to the opposite side thereof, thereby causing more complete conversion of said originally supplied hydrocarbon.

48. (original) The process of claim 47 wherein said sweep gas is passed counter current to the path of the vaporizable hydrocarbon.

49. (original) The process of claim 45 further comprising removing hydrogen from the opposite side of said membrane.

50. (original) The process of claim 40 wherein said hydrogen that permeates said permeable membrane is recovered by a vacuum means, wherein when a vacuum is used to recover hydrogen, the inlet on the permeate side is not used because no sweep gas is required, and only the outlet is required.

51. (original) The process of claim 44 wherein said vaporizable hydrocarbon is selected from the group consisting of natural gas, methane, methanol, ethane, ethanol, propane, butane, light hydrocarbon having 1-4 carbon atoms in each molecule, light petroleum fractions, including naphtha at boiling point range of 120-400 °F, or diesel, kerosene or jet fuel atboiling point range of 350-500 °F, or gas oil at boiling point range of 450-800 °F, hydrogen, carbon monoxide and mixtures thereof.

52. (original) The process of claim 44 wherein said vaporizable hydrocarbon consists essentially of methane.

53. (original) The process of claim 40 wherein said stream of vaporizable hydrocarbon includes carbon and steam at a minimum overall O:C ratio of 2:1.

54. (original) The process of claim 40 wherein said reforming chamber is at a temperature in the range of from about 300 to about 650°C.

55. (original) The process of claim 54 wherein said reforming chamber is at a temperature in the range of from about 400 to about 550 °C.

56. (original) The process of claim 55 wherein the temperature range permits the use of less expensive materials in construction.

57. (original) The process of claim 56 wherein said reforming chamber is constructed of less expensive materials, containing less chromium and nickel, not suitable for similar steam methane reformers in the art which must operate at higher temperatures.

58. (original) The process of claim 55 wherein said reforming chamber is constructed of an alloy containing less than 25% Cr and less than 20% Ni, with most of the balance comprising iron.

59. (original) The process of claim 55 wherein the reforming chamber is constructed of AISI 304 stainless steel, comprising about 18% Cr, about 8% Ni, and the balance Fe or AISI 316 L stainless steel.

60. (original) The process of claim 40 wherein said reforming chamber is at a pressure at a minimum of one bar absolute.

[62.] 61. (currently amended) The process of claim 41 wherein said reforming chamber is at a pressure in the range of 1 to 200 Bar.

62. (original) The process of claim 42 wherein the reforming chamber is at a pressure in the range of 10-100 Bar.

63. (original) The process of claim 40 wherein said reforming catalyst comprises at least one Group VIII transition metal.

64. (original) The process of claim 63 wherein said reforming catalyst comprises nickel.

65. (original) The process of claim 64 wherein said reforming catalyst is on a support.

66. (currently amended) The process of claim 65 wherein said support is selected from the group consisting of oxides, carbides, [or] and nitrides of Group III A , IIIB, IV A, IVB, [or] and Group VIII metals of the Periodic Table.

67. (original) The process of claim 66 wherein said support is selected from the group consisting of porous metal oxides that are inert on their own and porous metal oxides that have the capacity to passivate the surface of a support.

68. (original) The process of claim 67 wherein the support is a porous metal oxide.

69. (original) The process of claim 68 wherein the support comprises alumina.

70. (original) The process of claim 69 wherein said reforming catalyst comprises nickel on alumina.

71. (original) The process of claim 40 wherein said hydrogen-permeable membrane comprises one or more Group VIII transition metals or alloys thereof.

72. (original) The process of claim 40 wherein said vaporizable hydrocarbon is syngas.

73. (original) The process of claim 72 wherein said hydrogen permeable-membrane is situated on a porous ceramic or porous metallic support.

74. (original) The process of claim 73 wherein the support comprises a porous metal.

75. (original) The process of claim 73 wherein the support comprises a porous ceramic.

76. (original) The process of claim 75 wherein the support comprises alumina.

77. (original) The process of claim 74 wherein the support comprises porous stainless steel or Inconel or Hastelloy.

78. (original) The process of claim 77 further comprising an intermediate layer between said support and said membrane.

79. (original) The process of claim 75 further comprising the support serves as a thermal insulating layer to assist in keeping the membrane at a desired temperature.

80. (original) The process of claim 76 further comprising the concentration of alumina permits the tailoring of the design to emphasize insulating or conducting properties.

81. (currently amended) The process of claim 71 wherein said hydrogen-permeable membrane is selected from <u>the group consisting of</u> palladium and palladium alloys.

82. (original) The process of claim 81 wherein said hydrogen-permeable membrane comprises at least one of an alloy of Pd with 30-50 wt% copper, an alloy of Pd with 5-30 wt% silver, an alloy of Pd with 1-10 wt% yttrium, an alloy of Pd with 1-10 wt% holmium, an alloy of Pd with 1-10 wt% gold, an alloy of Pd with 1-10 wt% ruthenium, and an alloy of Pd with 1-10 wt% cerium.

83. (currently amended) The process of claim 71 wherein said hydrogen-permeable membrane is selected from <u>the group consisting of</u> platinum and platinum alloys.

84. (original) The process of claim 72 wherein said membrane has a thickness in the range of 10 Angstroms to 150μm.

85. (original) The process of claim 72 wherein said membrane has a thickness in the range of 0.1 to 20μm.

86. (original) The process of claim 81 wherein said membrane has a thickness in the range of 0.5 to 3 μm.

87. (original) The process of claim 40 wherein said membrane has a permeability in the range of 8×10^{-4} to 80 standard cubic meters/m^2/sec/bar ^{½}.

88. (original) The process of claim 87 wherein said membrane has a permeability in the range of 8×10^{-3} to 70 standard cubic meters/m^2/sec/bar ^{½}.

89. (original) The process of claim 40 wherein the use of said membrane permits fewer unit operations in the process.

90. (original) The process of claim 40 characterized in that nitrogen oxide formation is reduced to a level below 10 ppm.

91. (original) The process of claim 90 wherein nitrogen oxide formation is reduced to a level below 1.0 ppm.

92. (original) The process of claim 91 wherein nitrogen oxide formation is reduced to a level below 0.1 ppm.

93. (original) The process of claim 40 wherein said flameless distributed combustion comprises:

a) passing an oxidant through said inlet to a mixing point;
b) passing fuel gas through said corresponding inlet to a mixing point within the pathway between the two inlets juxtapose to the point to be heated;
c) preheating either the fuel gas or oxidant or both such that the temperature of the mixed stream exceeds an autoignition temperature of the mixture of the streams; and
d) combining the preheated oxidant and fuel gas at the mixing point resulting in autoignition forming combustion products.

94. (original) The process of claim 93 wherein said flameless distributed combustors further comprise:

a) an axial combustion chamber in communication with an inlet for oxidant at one end and in communication with a combustion product outlet at the other end;

b) a fuel conduit within the axial combustion chamber, the fuel conduit defining a fuel volume, the fuel volume in communication with the fuel supply, and in communication with the combustion chamber through a plurality of orifices along the fuel conduit wherein the fuel conduit comprises an electrically conductive material; and

c) any method of preheating air effective to heat the fuel conduit in the vicinity of at least one orifice to temperature above a temperature at which the fuel will ignite when the fuel passes through the orifices.

95. (original) The process of claim 40 further comprising said section containing said membrane is packed with a methanation catalyst to react with any trace amounts of CO that escape through said membrane.

96. (original) The process of claim 95 wherein said methanation catalyst is nickel or iron or copper based.

97. (original) The process of claim 40 further comprising said steam reformer can function alone as a hydrogen generator to supply a source of hydrogen for any process requiring a source of hydrogen.

98. (original) The process of claim 97 wherein said steam reformer can function alone as a hydrogen generator to supply a source of hydrogen for any process selected from the group consisting of production of ammonia, production of electricity, refining, semiconductor processing, hydrogen peroxide manufacture,

hydrogenation of chemical intermediates and production of hydrogen for chemical analytical testing.

99. (original) A process for the production of pure hydrogen and the use thereof in a zero emission hybrid power system which comprises:

a) Providing a generally tubular reforming chamber having one or more inlets for a vaporizable hydrocarbon and steam and one or more corresponding outlets for byproduct gases, including H_2O and CO_2, with a flow path in between said inlet and outlet,
   and one or more inlets for and corresponding outlets for sweep gas and hydrogen, with a flow path between said inlet and outlet, and
   an inlet for preheated air and a corresponding inlet for fuel gas mixtures, with a flow path between said inlets containing a plurality of flameless distributed combustion heaters,
   wherein said flow path for vaporizable hydrocarbon and flow path for sweep gas form two concentric sections with an annulus between having a reforming catalyst therein and a hydrogen permeable membrane on the inside or outside of one of the concentric sections;
b) Feeding into said reforming chamber through said inlets a vaporizable hydrocarbon and steam;
c) Flowing said vaporizable hydrocarbon over said reforming catalyst;
d) Causing steam reforming to take place in said reforming chamber;
e) Conducting said reforming in the vicinity of a hydrogen permeable and hydrogen-selective membrane, whereby pure hydrogen permeates said membrane;

f) directing said pure hydrogen to the anode of a fuel cell and directing by-product gases to the cathode of said fuel cell;

g) Wherein heat to drive the reaction in said reforming chamber is provided by said flameless distributed combustion.

100. (original) The process of claim 99 wherein steam, carbon dioxide, nitrogen, or a condensable hydrocarbon is used as a carrier of hydrogen.

101. (original) The process of claim 100 wherein the fuel cell is a high-pressure fuel cell.

102. (original) The process of claim 101 wherein the fuel cell is a high-pressure molten carbonate fuel cell.

103. (original) The process of claim 102, which further comprises the separation and sequestration of high concentrations of carbon dioxide from the process streams and/or from other external CO_2-containing streams.

104. (original) The process of claim 103 wherein said carbon dioxide is used to make chemicals.

105. (original) The process of claim 99 wherein the carbon dioxide stream, the hydrogen stream or the nitrogen stream from the process is used to make urea, ammonia or ammonium sulfate.

106. (original) The process of claim 40 wherein said carbon dioxide is used in oil recovery.

107. (original) The process of claim 103 wherein said carbon dioxide is used in oil recovery.

108. (original) The process of claim 40 wherein the carbon dioxide is used in coal beds.

109. (original) The process of claim 103 wherein said carbon dioxide is used in coal beds.

110. (original) The process of claim 40 wherein the carbon dioxide is used in secondary or tertiary oil recovery.

111. (original) The process of claim 103 wherein the carbon dioxide is used in secondary or tertiary oil recovery.

112. (original) The process of claim 99 which produces essentially negligible amounts of NO_x.

113. (original) The process of claim 112 wherein the NO_x formation is reduced to a level below 10 ppm.

114. (original) The process of claim 113 wherein the NO_x formation is reduced to a level below 1.0 ppm.

115. (original) The process of claim 114 wherein the NO_x formation is reduced to a level below 0.1 ppm.

116. (original) The process of claim 102 wherein the presence of negligible amounts of NO_x greatly enhances performance and efficiency of said method.

117. (original) The process of claim 99 further characterized by a material and energy efficiency advantage comprising a tight material and energy integration between the Membrane Steam Reforming reactor (MSR) and the Molten Carbonate Fuel Cell (MCFC) characterized by:

a) Feeding carbon dioxide made in the FDC heater and the membrane steam reformer to the molten carbonate fuel cell;

b) Recycling the water used as membrane steam reformer sweep gas plus water made in the molten carbonate fuel cell, back to the membrane

steam reformer feed, thus, reducing water emissions to a minimum purge stream, and obviating the need of a fresh water supply;

c) Using the pressure and temperature of specific outlet streams to generate electricity in turbines, instead of resulting in waste heat; and

d) Using the enthalpy of specific outlet streams to exchange heat with given inlet streams for reduction in net fuel usage.

118. (original) The process of claim 40 further characterized by advantages in terms of distributed production of hydrogen on demand without storage requirements.

119. (original) The process of claim 99 further comprising the option of using a vaporizable hydrocarbon produced in a remote location to produce electricity for transportation to nearby residential or commercial markets instead of transporting by pipeline.

120. (original) The process of claim 119 wherein the vaporizable hydrocarbon is natural gas.

121. (original) The process of claim 40 wherein the high purity hydrogen stream produced is used in a PEM fuel cell to generate electricity.

122. (original) The process of claim 40 wherein the fuel fed to the FDC heaters is hydrogen.

123. (original) The process of claim 122 wherein the fuel fed to the FDC heaters is hydrogen and it is combusted with air, at the stoichiometric ratio to oxygen of 2:1, resulting in a flue gas steam that is pure in nitrogen on dry basis.

124. (currently amended) The process of claim 99 wherein nitrogen is obtained as a high purity [steam] <u>stream</u> from the outlet of the cathode of the molten carbonate fuel cell.

125. (original) The process of claim 124 wherein nitrogen is used for any process requiring a source of nitrogen.

126. (original) The process of claim 124 wherein nitrogen is used for any process selected from the group consisting of production of ammonia, nitric acid, urea and ammonium sulfate.

127. (currently amended) The process of claim 40 wherein carbon dioxide is used for any process selected from the group consisting of production of urea [or], building materials [or], food products[or]and carbonated drinks.

128. (original) The process of claim 41 wherein the FDC section does not have a fuel inlet, but rather uses the permeated hydrogen is used as a fuel in the FDC heating section with air or oxygen as the oxidant.

129. (currently amended) The process of claim 1 wherein between 90 and 95% of the heat generated by flameless distributed combustion [in the heating zone] is transferred to the reacting fluids in said reaction zone.

130. (original) The process of claim 1 wherein the vaporizable hydrocarbon comprises partly or entirely of a syngas stream from a Catalytic Partial Oxidation process.